

Equilibrium in the Reaction of Hydrogen with Ferrous Oxide in Liquid Iron at 1600 Degrees Cent.

By M. G. Fontana and John Chipman



Abstract of a Dissertation Submitted in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy at the University of Michigan

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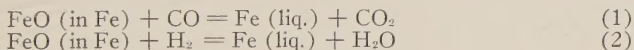
EQUILIBRIUM IN THE REACTION OF HYDROGEN WITH FERROUS OXIDE IN LIQUID IRON AT 1600 DEGREES CENT.

BY M. G. FONTANA AND JOHN CHIPMAN

Abstract

A careful experimental study of the reaction of hydrogen with dissolved ferrous oxide in liquid iron has led to the discovery and elimination of a source of error which had affected the accuracy of results previously reported. It is found that the equilibrium constant of the reaction is a true constant at all oxygen concentrations up to saturation. The results are used to obtain the free energy of ferrous oxide at 1600 degrees Cent. (2910 degrees Fahr.). Calculations show that the results of this investigation constitute a confirmation of Vacher's experiments on the iron-carbon-oxygen system.

THE reactions involving ferrous oxide in liquid steel are of sufficient importance to justify the expenditure of considerable time and effort in determining the exact behavior of this substance under conditions of equilibrium. A number of its reactions have been investigated in some detail and their equilibrium constants are now known with a fair degree of approximation. Among the simplest and most useful of these studies have been those in which the dissolved ferrous oxide was brought into equilibrium with a controlled gaseous atmosphere as illustrated in the following equations:



Both of these reactions were investigated by Vacher (1)¹ and the second was studied in somewhat more detail by Chipman (2).

¹The figures in parentheses refer to the bibliography appended to this paper.

This paper is taken from a dissertation submitted by M. G. Fontana in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Michigan. Dr. Fontana is now assistant metallurgist with E. I. du Pont de Nemours and Company, Wilmington, Delaware. Dr. Chipman was Research Engineer, Department of Engineering Research, University of Michigan, and is now Associate Director of the Research Laboratories, American Rolling Mill Company, Middletown, Ohio.

remove free oxygen. From this furnace the hydrogen passed through an orifice flowmeter, E, and then through the saturators and into the furnace. D is the by-pass outlet that was used while melting or heating the iron under hydrogen. In this case D was connected to the inlet K by means of rubber tubing which had a pinch clamp on it near D to regulate the flow of gas.

The preliminary saturator F consisted of a liter side-arm flask partially filled with water and heated by a resistance heater to approximately the same temperature as the saturator G. The latter consisted of three vertical towers, the first two packed with broken glass and the third empty to serve as an entrainment separator. This assembly was made of pyrex glass and was welded together so that no rubber connections were necessary. It was immersed in a thermostat consisting of a large battery jar, which was filled with transformer oil. The oil was vigorously stirred by means of an immersed paddle which was driven by an electric motor. The outside of the jar was well insulated to cut down the heat loss and to insure better temperature control. The heating coil had a variable resistance in series by means of which the temperature was manually controlled to less than ± 0.1 degree Cent. The temperature was measured by means of a 40-100 degrees Cent. (105-210 degrees Fahr.) thermometer calibrated against a standard thermometer from the U. S. Bureau of Standards.

The performance and efficiency of the saturator under various conditions were checked by passing the gas mixtures through a weighed tube containing dehydrite and phosphorus pentoxide to absorb water which was determined by the gain in weight. The hydrogen was collected over water and determined volumetrically. The saturator temperature, the flask temperature, the rate of hydrogen flow and the conditions in the entrainment chamber were varied. The results showed complete saturation under all of these conditions.

Fig. 2 shows a section of the furnace set-up used in the equilibrium work. The silica tube was surmounted by a brass head which was cemented securely with zinc cement. The sight glass was of pyrex and was held loosely in position by means of a slit brass ring. One turn of previously burned asbestos cord served as a gasket. This arrangement also provided a safety valve to take care of any explosions that might have occurred in the furnace. The sight glass was raised from the furnace head proper by means of a brass tube extension which was water cooled to prevent fogging of the sight

glass which otherwise would have been a source of trouble. There was not sufficient cooling, however, to cause condensation of water vapor.

The iron was melted in a magnesia crucible which rested on a magnesia base. For certain runs in which the crucible containing the liquid iron was to be quenched directly into a bath of tin or water,

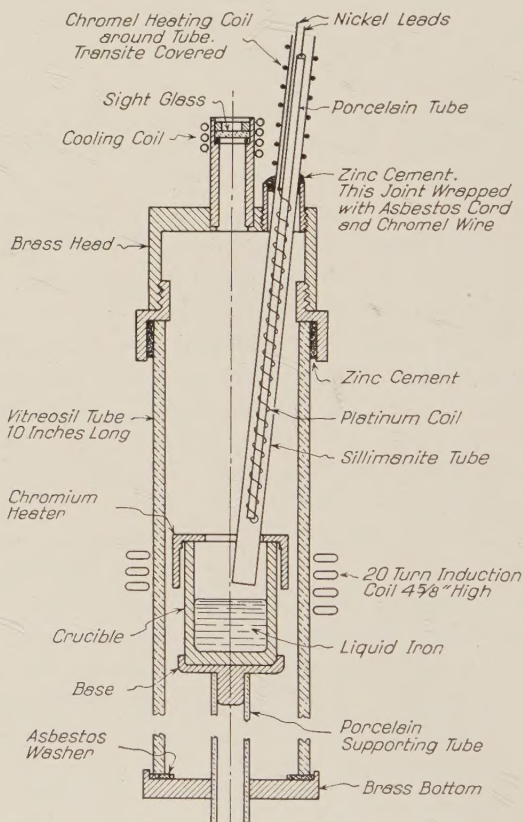


Fig. 2—Cross Section of Furnace Setup Used in this Investigation.

the base was not used. For these runs the crucible was formed with a lower projection which fitted directly into the supporting tube. A crucible of this type is shown in the extreme left of Fig. 3. A soft brick washer was used to separate the crucible from the porcelain tube to avoid overheating the latter and so that it would not crack

when it was immersed into the water. The base and several crucibles are shown in Fig. 3. The chromium heater, which will be discussed later, rested directly on the crucible as shown in Fig. 2. The heater had an elliptical hole in it through which the sillimanite inlet tube passed and through which the optical pyrometer was sighted. The whole internal furnace set-up was supported from the bottom by means of a porcelain tube. The seal between the furnace bottom and

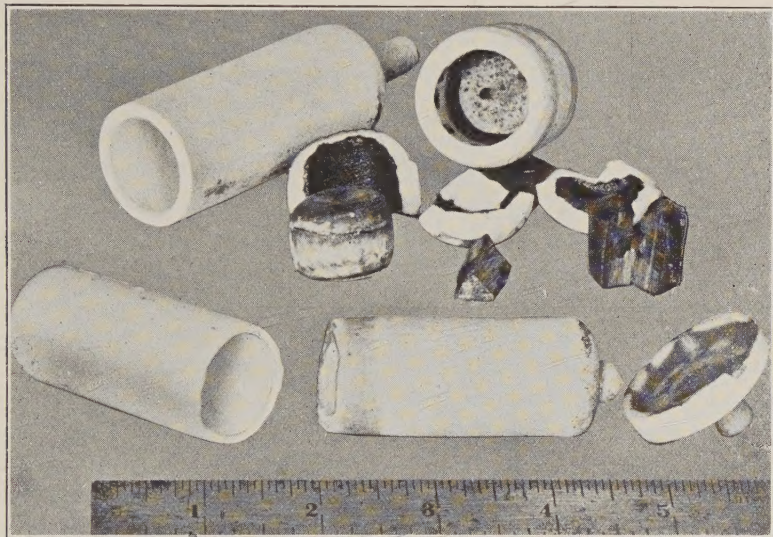


Fig. 3—Typical Crucibles and Ingots Used in this Investigation.

the supporting tube was made with asbestos cord. An asbestos washer was placed between the brass bottom and the quartz tube. The power for the 20-turn induction coil was furnished by a 35 Kva. high frequency converter. The temperature of the chromium heater was varied by raising or lowering its position with respect to the top of the induction coil.

Magnesium oxide was used for the manufacture of the crucibles because it is not easily reduced and possesses the very desirable property of absorbing several times its own weight of iron oxide without seriously impairing its use as a refractory. Beryllium oxide was tried and gave more satisfactory results than magnesium oxide but its high cost precluded its extensive use. A mix consisting of one part of ball-milled powder and two parts of 60 mesh yielded the

best crucibles. The crucibles were formed dry by tamping in a graphite mold around a steel core. After removing the core and covering each mold with a graphite top seven of the crucibles were simultaneously fired in an induction furnace to about 2000 degrees Cent. (3630 degrees Fahr.). Crucibles produced in this manner were easily made, were hard and dense, and possessed remarkable strength.

The electrolytic iron which was used throughout this investigation was first melted and cast into 0.9-inch round bars. Pieces of these bars weighing about 50 grams were each melted in a crucible under a pressure of 0.05 millimeters or less. The crucible containing its vacuum-melted charge was then used for an equilibrium run. The reasons for vacuum melting were to remove nitrogen and carbon and to prepare a charge of iron that could be readily melted down without great danger of bridging or of overheating the chromium heater. After the equilibrium run "pie slices" were cut from the ingot and analyzed for oxygen in an improved vacuum fusion apparatus. This is unquestionably the best method for determining oxygen in ingots of this type. Ingots and the manner of sampling are illustrated in Fig. 3.

The temperature of the liquid iron was measured by means of an optical pyrometer of the disappearing filament type which was sighted through a prism and the sight glass in the furnace head. This previously calibrated instrument was checked during each run by observing the melting point of iron by reducing the power input into the furnace so as to cause a slow solidification of the metal. The melting point of iron containing low oxygen was taken to be 1530 degrees Cent. (2785 degrees Fahr.) while that of iron saturated, or nearly saturated, with oxygen was assumed to be 1525 degrees Cent. (2775 degrees Fahr.) as reported by Tritton and Hanson (3). The measurement of the temperature of the liquid iron represents the greatest source of uncertainty in this work. The temperature of the melt was regulated by carefully controlling the power input to the furnace. Practically all of the experiments were made at 1600 degrees Cent. (2910 degrees Fahr.), but for those runs made in the neighborhood of that temperature the equilibrium constant was corrected to 1600 degrees Cent. (2910 degrees Fahr.) by means of the approximate temperature coefficient for the reaction as observed by Chipman (2).

Early developments during this investigation indicated that the degree of preheating the gases had a decided effect upon the equi-

librium as will be explained below. The preheating arrangement is partially shown in Fig. 1. The first three heaters H, I, and M consisted of chromel wire wound around the tubing. M was covered with transite and kept at a red heat. The sillimanite inlet tube contained a platinum coil as shown in Fig. 2. The temperature of the coil was determined by measuring its resistance, and calibration by this method gave the average temperature of the coil. The chromium heater as shown in Fig. 2 heated the upper portion of the crucible and part of the exit end of the inlet tube. The temperature of the heater was estimated to be 1600 degrees Cent. (2910 degrees Fahr.) during the run. The gases were also preheated by radiation from the liquid metal itself.

Chromium was chosen for the construction of the heater because of its high melting point and good resistance to oxidation. Considerable trouble was encountered before a sound and easily machinable casting was produced. Several molds and molding materials were tried with poor success before the mold that yielded good castings consistently was devised. This consisted of a two-piece steel mold with an inverted magnesia crucible for a core. The crucible was held firmly centered by means of a screw and a hole in the mold allowed the expanding gases in the crucible to escape. Electrolytic chromium was used and it was melted in a 400-gram induction furnace constructed especially for that purpose. A graphite heater was first tried but it caused considerable fogging of the sight glass and also reacted with the water vapor present to form carbon monoxide. The absorption of this gas by the melt resulted in hollow ingots with low oxygen contents.

PROCEDURE

The hydrogen train and the saturators were thoroughly flushed out with purified gas for about two hours before the power was turned on to the furnace. The furnace was flushed out with hydrogen for at least fifteen minutes before the heating of the metal began. The iron was sometimes melted under hydrogen and sometimes under saturated, or partially saturated, hydrogen. After the iron had completely melted, the power input was reduced and the melting point of the iron determined during its slow solidification. The power was then increased and the hydrogen was passed through the saturator at the desired rate of flow. The beginning of the run was marked by the time when the furnace temperature "settled

down" at 1600 degrees Cent. (2910 degrees Fahr.) and the run was continued for about 45 minutes.

The iron was cooled in position in the furnace by simply turning off the power or it was quenched for a more rapid rate of cooling. The time required for solidification in position was about fifteen seconds and most of the ingots were cooled in this manner. Several attempts were made to lower the crucible into a bath of liquid tin contained in the bottom of the furnace, but they were not completely successful. The most rapid cooling was obtained when the crucible was lowered directly into a large bath of water at the end of the run. The furnace power was not turned off during this operation and the time required to get the crucible completely immersed in water was only about one second. The crucible was lowered vertically into the water so that the metal would not run out.

EXPERIMENTAL RESULTS

A total of forty ingots were prepared during this investigation and a summary of all of the data that are considered reliable is shown in Table I. Since a large part of this work was concerned with developing a furnace set-up and technique, some of the runs were made to determine the effects of variables in the procedure and their results are not included in determining the equilibrium constant. In addition, several ingots were rejected because of uncertain temperature measurement chiefly due to fogging of the sight glass. Several were discarded because of air leaks as evidenced by high nitrogen content (0.002 per cent or higher) of the ingot, and others because of carbon monoxide evolution resulting in hollow ingots in the runs wherein the graphite heater was used.

The second column of Table I gives the ratio of steam to hydrogen in the furnace as computed from the barometric pressure and the vapor pressure of water in the saturator, and corrected for the small deviation of steam from the ideal gas law. The third column gives the temperature during the final 30 to 45 minutes of each run. The fourth contains the average of duplicate or triplicate oxygen determinations.

The equilibrium constant of Reaction 2 may be most simply expressed by the following equation:

$$K' = \frac{(\text{H}_2\text{O})}{(\text{H}_2) (\% \text{ O})}$$

The observed value of K' is recorded in the fifth column of the table while the sixth shows the constant corrected to 1600 degrees Cent. (2910 degrees Fahr.) by means of the approximate temperature coefficient previously established (2). The column contains data as to the method of preheating the gas stream which will be discussed in the following paragraphs.

Table I
Heats and Equilibrium Data

Heat Number	H ₂ O	Temp. °C.	Per Cent Oxygen	K' Observed	K' 1600	Preheat
	H ₂					
33	0.259	1620	0.061	4.25	4.58	None
34	0.259	1620	0.065	4.00	4.33	Pt. coil
35	0.259	1625	0.068	3.82	4.23	Pt. coil
37	0.124	1620	0.030	4.10	4.43	Pt. coil
40	1.021	1600	0.211	***	***	Pt. coil
51	0.263	1600	0.062	4.20	4.20	Coil + Cr heater
52	0.263	1590-95	0.063	4.16	4.04	Coil + Cr heater
53	0.263	1600	0.067	3.94	3.94	Coil + Cr heater
55	0.260	1600	0.060	4.31	4.31	Pt. coil
57	0.847	1505	0.222	3.82	3.90	Pt. coil
58	0.754	1600	0.184	4.10	4.10	Coil + Cr heater
59	0.723	1600	0.188	3.84	3.84	Coil + Cr heater
60	0.755	1600	0.190	3.98	3.98	Coil + Cr heater
62*	1.414	1600	0.215	***	***	Coil + Cr heater
63*	0.980	1600	0.196	***	***	Coil + Cr heater
64*	0.983	1600	0.200	***	***	Coil + Cr heater
67	0.671	1600	0.162	4.14	4.14	Coil + Cr heater
69	0.715	1595	0.196	3.66	3.58	Coil + Cr heater
70**	0.829	1605	0.209	3.96	4.04	Coil + Cr heater

*Quenched in tin.

**Quenched in water.

***See Fig. 4.

Effect of Preheating the Gases on the Equilibrium

The results of a series of experiments carried out during this investigation showed that the degree of preheating the gases had a decided effect upon the equilibrium. These experiments were prompted by the existence of several apparent anomalies. The first was that the preliminary runs at low oxygen concentration did not check the previous results obtained in this laboratory in that our new results showed appreciably lower values for the equilibrium constant. The second was that the observed ratio of steam to hydrogen was consistently higher than that calculated from the ratio $\text{CO}_2:\text{CO}$ as found by Vacher and Hamilton (4) in equilibrium with iron of equal oxygen content. Our suspicions were further heightened by the surprising results reported by Emmett and Shultz (5) in which they observed a thermal separation of steam and hydrogen even in a flow-

ing system and at temperatures considerably below the melting point of iron.

The hypothesis presented by the writers (6) to explain the observed phenomenon is based on the well known concentration gradient that exists in solutions or gaseous mixtures when a temperature gradient is present. The heavier gas will be present in greater concentration in the cold region. The greater the ratio of the molec-

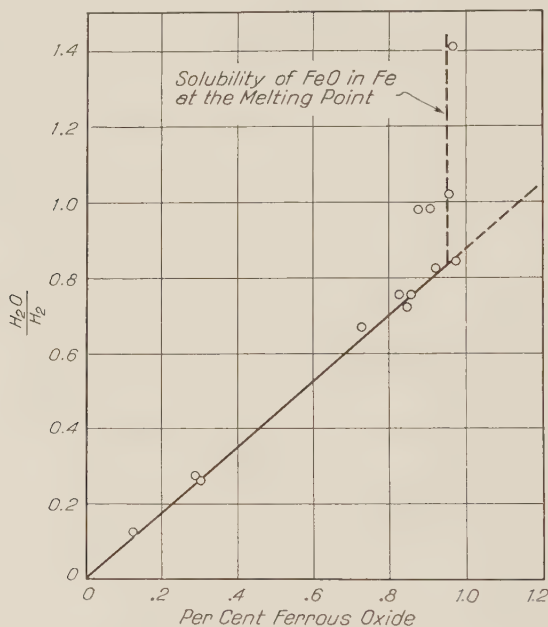


Fig. 4—Relationship Between Steam — Hydrogen Ratio and Oxide Content of the Melt.

ular weights of the gases mixed, the more pronounced the “segregation” should be for a given temperature gradient (7). This effect should be quite pronounced, therefore, in the system H_2 - H_2O -liquid Fe but should not offer appreciable interference in the system CO_2 - CO -liquid Fe. When the preheating of the gases is accomplished only by radiation from the liquid iron, a large temperature gradient will exist in the region adjacent to the iron and considerable thermal diffusion will occur. For a given ratio of $H_2O:H_2$ the concentration of H_2O will be greater in the colder region or the region further from the melt, whereas the hydrogen would tend to diffuse towards the liquid metal, and the ingot would, therefore, contain less oxygen

than it would contain if there were no "segregation" of the gases. The ideal conditions, or those which would be conducive to the existence of true equilibrium, would be attained if the gases were at the same temperature as the metal when they came in contact with the metal. Eastman and Ruben (8) have recently upheld our views on thermal diffusion in a dynamic system.

It should be possible to diminish the temperature gradient and thereby also the amount of thermal separation by preheating the gas stream as it approaches the hot metal surface. The preheating due to radiation from the liquid iron will be more efficient the lower the lineal velocity of the gases. The reason for the lower results in this work when compared to those previously reported for a given rate of flow and ratio $H_2O:H_2$, can thus be explained by comparing the sizes of the inlet tubes. In the former investigation a 3-millimeter diameter inlet tube was used, whereas we used a 7-millimeter tube, thus obtaining lower velocity of flow, better preheating of the gases and attendant higher oxygen contents of the ingots. Vacher used a lower rate of flow and a larger tube and obtained still higher oxygen contents.

The results of the heats which were made to determine the effect of preheating the gases are shown in Table II. The amount of preheat was varied by using the chromium heater described above and the platinum resistance heater inside the inlet tube. The temperatures of the chromium heater are estimates. The results indicate that the effect is greatest in the first stages as the preheating increases. Decreasing the rate of flow from 300 cubic centimeter of dry hydrogen per minute to 200 cubic centimeters has a slight effect upon the constant. It is believed that the preheating in experiments 52 and 53, especially the latter, has been sufficient to largely eliminate

Table II
Equilibrium at 1600 Degrees Cent and 0.065 Per Cent Oxygen

Heat Number	(H ₂ O)	Flow cc/min.	Pt. Coil Temp. °C.	Preheat Conditions
	(H ₂) × % O			
1-18*	4.75	300		3 mm. tube
33	4.58	300		7 mm. tube
34	4.33	300	1170	No Cr heater
35	4.23	300	1320	No Cr heater
51	4.20	300	1170	Cr heater 1500° C.
52	4.04	300	1170	Cr heater 1600° C.
53	3.94	200	1170	Cr heater 1600° C.
55	4.31	450	1050	No Cr heater

*Reference (2).

the source of error due to thermal diffusion. Subsequent heats were made at a rate of flow of 200 cubic centimeters per minute or under conditions similar to heat number 53.

The Criteria of Equilibrium

In addition to reaching a constant value of K' after sufficient preheating of the gases had occurred, another criterion of equilibrium was that the oxygen content of the iron reached a constant and reproducible value at a constant steam-hydrogen ratio. In the previous investigation it was found that 15 minutes was sufficient time to secure equilibrium for the oxygen concentrations of 0.01 and 0.11 per cent on which the effect of time was investigated. This rapid attainment of equilibrium is doubtless chiefly due to the fact that the iron is constantly and vigorously stirred in the high frequency induction furnace.

Most of the heats in this work were run for about 45 minutes under constant temperature, preheat, flow and steam-hydrogen ratio. At high concentrations of oxygen in the iron, the iron oxide reacts with the magnesia crucible and some of the oxygen is removed from the melt. This fact had to be considered in the ingots that were nearly saturated with iron oxide. An examination of the pieces of crucible in Fig. 3 will show the attack on the crucible by the oxide from the melt. If this reaction occurred continuously, equilibrium would never be obtained because oxygen would be continually removed from the metal. This condition, however, is not probable because of the sharp temperature gradient that exists between the liquid iron and the crucible. After some attack has occurred the outer surface of the slag layer solidifies and further slag formation is stopped. Examination of a high oxygen ingot after a run will support this contention. The surface of the crucible adjacent to the iron is bright and shiny and the ingot does not stick to the crucible wall.

Two runs were made to be sure that the attack on the crucible did not affect the equilibrium under the conditions of our experiments. Heat No. 69 was run for almost two hours and allowed to solidify in position in the furnace. This ingot contained about 0.2 per cent oxygen. Examination of Fig. 5 will show the results on this run. It will be noticed that the constant is below the line drawn for K' thus indicating a higher oxygen content. This shows that

the effect of the crucible attack, which tends to lower the oxygen content, has not affected the result in this case and probably has been entirely eliminated in all of the heats made. Heat No. 70, which was quenched in water, was run for $1\frac{1}{2}$ hours to yield an ingot of 0.21 per cent oxygen and also shows good agreement with the 45 minute runs.

The effect of the oxygen content of the charge on the equilibrium was investigated by approaching the equilibrium with higher oxygen and lower oxygen melts. This was done by subjecting the melt to

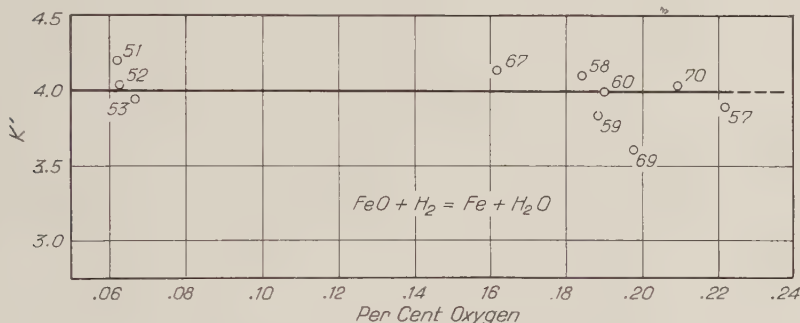


Fig. 5--Equilibrium Runs at Various Oxygen Concentrations.

a higher, or lower, steam-hydrogen ratio for some time before the desired ratio was maintained. Our experience showed that any effects due to this procedure were entirely eliminated during the 45 minutes allowed for each run under constant conditions.

Nature of the Solution of Oxygen in Iron

The completely straight line relationship between the steam-hydrogen ratios and the ferrous oxide content of the melt as shown in Fig. 4, affords a more rigorous proof than was formerly obtained that the oxygen dissolved in the liquid iron is present as an oxide containing one atom of oxygen. It also demonstrates that the solution of iron oxide in iron conforms more nearly to the ideal solution law than was previously reported.

An indication of the solubility of ferrous oxide in iron can be obtained from an examination of Fig. 4. At steam-hydrogen ratios higher than the ratio corresponding to about 1 per cent ferrous oxide, considerable ferrous oxide was ejected from the melt during solidification. Using ratios even as high as 1.4, the ferrous oxide

content of the ingot refused to exceed 1 per cent. The fact that the ferrous oxide content consistently stayed between 0.9 and 1.0 per cent may be considered as an indication of the maximum solubility of ferrous oxide in iron at the melting point. Tritton and Hanson (3) report 0.21 per cent oxygen (0.94 per cent FeO) as the solubility at the melting point. Herty (9) reports 0.22 per cent oxygen (0.98 per cent FeO). These figures are in good agreement with the data shown in Fig. 4. Herty reports the solubility of oxygen at 1600 degrees Cent. (2910 degrees Fahr.) as 0.305 per cent and Körber's (10) corresponding result is 0.325 per cent. This means that considerable ferrous oxide has to be thrown out of solution before the ingot solidifies in order to show only 0.21 per cent oxygen. The speed with which ferrous oxide is ejected as the melt cools is amazingly rapid since the time required for solidification of our ingots was very short as stated above. Confirmation of our conclusion that the excess ferrous oxide is thrown out of solution on cooling to the melting point was found in the microscopic examination of several of the ingots.

The Nature of Iron Oxide Inclusions in Iron

The large amount of ferrous oxide that is thrown out of solution as the melt cools, coalesces rapidly and tends to rise to the surface. Fig. 6 shows oxide inclusions near the top of heat 40. None of these large inclusions were found in the lower portion of the ingot, even though the time required for solidification from 1600 degrees Cent. (2910 degrees Fahr.) was only about twenty seconds. Note the very large inclusion that was trapped just as it reached the surface. Fig. 7 was taken on the middle of heat 70, and shows that the inclusions had formed but did not have time to rise to the surface. This ingot was quenched in water, and was probably completely solid in less than three seconds.

Although oxygen in liquid iron is always present as ferrous oxide, Figs. 6 and 7 show a duplex structure, which indicates the presence of another constituent. Chaudron (11) and Ffeil (12) have shown that ferrous oxide partially decomposes during cooling as follows:



The ferrous oxide first becomes saturated with Fe_3O_4 , and then ejects it as a separate phase as shown in the two figures. The dark



Fig. 6—Photomicrographs Showing Oxide Inclusions Near Top of Heat 40. $\times 100$.
Fig. 7—Photomicrographs Taken Near the Middle of Heat 70 Showing that the Inclusions Had Formed but Did Not Have Time to Rise to the Surface. $\times 300$. These Two Figures Show a Duplex Structure.

areas within the inclusions are probably Fe_3O_4 containing FeO and iron. The grey areas of the inclusions are probably FeO saturated with Fe_3O_4 and iron.

THERMODYNAMIC CALCULATIONS

Effect of Oxygen Concentration on the Equilibrium and the Activity of Ferrous Oxide

Fig. 5 shows that the equilibrium constant for the reaction studied does not vary with the oxygen content of the iron. The constant plotted is:

$$K' = \frac{(\text{H}_2\text{O})}{(\text{H}_2) (\% \text{O})}$$

The line represents a value of 3.95 for K' which was calculated as an average of the points shown except 51 which did not have sufficient preheating of the gases. The constant may be considered accurate to better than ± 0.2 , or about ± 5 per cent.

The fact that K' does not vary with oxygen concentration indicates that the reaction behaves according to the simple mass law. The activity of ferrous oxide is proportional to its concentration in the solution and this holds true not only in dilute solutions, as has been previously supposed, but also in all ranges of oxygen concentrations up to and including saturation. In the earlier work it was found that the equilibrium constant for the reaction decreased considerably with increasing oxygen concentrations indicating that the activity of the ferrous oxide did not increase as fast as the increase in ferrous oxide content of the melt. This apparent deviation of the behavior of the reaction from the laws of the ideal solution made it imperative, of course, that the activity of ferrous oxide, and not its concentration, be used when applying the mass law to reactions involving dissolved ferrous oxide. To facilitate this, a table of activity coefficients was deduced from the equilibrium measurements. Fig. 5, however, shows that the activity of ferrous oxide is equal to its per cent by weight at all concentrations. The per cent by weight will, therefore, be used in subsequent calculations.

Vacher (1) prepared four ingots by subjecting iron at 1580 degrees Cent. (2875 degrees Fahr.) to a mixture of steam and hydrogen. Our results, allowing for the difference in temperature, are well within the range of his observed equilibrium constants.

The Free Energy of Ferrous Oxide in Liquid Iron

From the equilibrium data obtained during this investigation, the free energy of ferrous oxide in liquid iron can be calculated. If we let the activity of liquid iron be equal to 1, and that of dissolved FeO be equal to its percentage, we may define the equilibrium constant for the reaction as

$$K = \frac{(H_2O)}{(H_2) (\% FeO)}$$

This constant is directly related to the standard change of free energy for the reaction. The relationship is:

$$\Delta F^\circ = -RT \ln K = -4.575 T \log K$$

where ΔF° is the change in free energy in the reaction when each substance is in a standard state (that is, when its activity = 1), T is the temperature in degrees Kelvin (absolute) and $\ln K$ and $\log K$ are the natural and ordinary logarithms, respectively, of the equilibrium constant of the reaction.

The expression for K is similar to that used above for K' , except that we are now expressing oxygen content as per cent FeO instead of per cent oxygen. K is, therefore, equal to $K'/4.49$, the average value of which, as found in Table I, is 0.88 at 1600 degrees Cent. (2910 degrees Fahr.), or 1873°K. The change in free energy for the reaction is, therefore:



The free energy of steam at this temperature quoted from the previously published work (13) is:

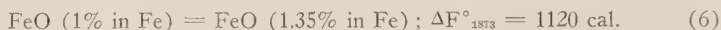


By combining Equations 3 and 4, we obtain the free energy of formation of dissolved ferrous oxide at 1600 degrees Cent. (2910 degrees Fahr.):

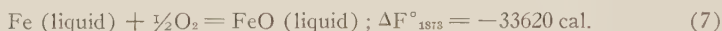
*The Free Energy of Liquid Ferrous Oxide*

It is desirable to know the free energy of pure liquid ferrous

oxide for thermodynamic calculations on slag reactions. We may justly assume that the free energy of liquid ferrous oxide is approximately equal to its free energy in the saturated solution. The solubility of ferrous oxide in iron at 1600 degrees Cent. (2910 degrees Fahr.) from the data of Herty (9) and of Körber (10) is 1.35 per cent. The change in free energy in going from a 1 per cent solution to a 1.35 per cent solution is $4.575 T \log 1.35$. This may be represented as follows:

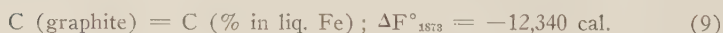
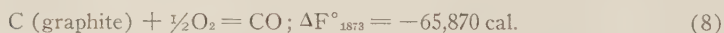


Now Equations 5 and 6 may be combined to obtain a figure which represents the free energy of FeO in the saturated solution, and which, therefore, is very close to the free energy of pure liquid ferrous oxide.



The Carbon-Oxygen Equilibrium in Liquid Iron

Because of its fundamental importance, the carbon-oxygen equilibrium has been the subject of many investigations. The reaction and its equilibrium constant are obtained by combining Equation 5 with the following equations and free energy values at 1600 degrees Cent. (2910 degrees Fahr.), which were derived in the previous work (13).



The results of the combination are:



The equilibrium constant at 1600 degrees Cent. (2910 degrees Fahr.) is then:

$$\frac{(\text{per cent FeO}) (\text{per cent C})}{(\text{CO})} = 0.006$$

This result is in good agreement with Vacher's (1) experimentally determined value of 0.010 which perhaps represents the best experimental research on the carbon-oxygen equilibrium. It

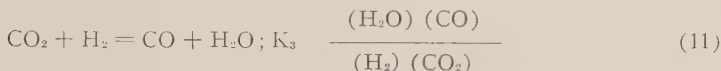
is of interest to note that the calculated and experimental values of this constant are becoming more nearly equal. Of course, the experimental value should be given preference.

The Water Gas Reaction

The equilibrium constants for the reactions represented by equations (1) and (2) can be expressed respectively as follows:

$$K_1 = \frac{(\text{CO}_2)(\text{Fe})}{(\text{CO})(\text{FeO})} \text{ and } K_2 = \frac{(\text{H}_2\text{O})(\text{Fe})}{(\text{H}_2)(\text{FeO})}$$

If we divide K_2 by K_1 , we get the equilibrium constant, K_3 , for the water gas reaction thus:



The above constants are expressed differently than K' in order that they may be directly compared to previously published data wherein the mol fractions of the reacting substances have been employed in the expressions for the equilibrium constants.

Let us calculate the equilibrium for reaction (11) using Vacher's data on the Fe-O-C system and the authors' data on the Fe-O-H system. Vacher reports 27.0 as his best value for K_1 at 1580 degrees Cent. (2875 degrees Fahr.) at which temperature his work was carried out. Since the temperature coefficient for this reaction is not well known in this range, we will convert the data for K_2 to 1580 degrees Cent. (2875 degrees Fahr.), using the temperature coefficient referred to above. The corrected value for K' at 1580 degrees Cent. (2875 degrees Fahr.) is 3.62. When the ferrous oxide concentration is expressed as mol fraction rather than as per cent oxygen, the value for K_2 at 1580 degrees Cent. (2875 degrees Fahr.) then becomes 103.5.

Dividing K_2 by K_1 , we get a value of 3.83 for K_3 , the equilibrium constant for the water gas reaction. Bryant (14) reviewed all of the published data on this reaction and computed the equilibrium constants at temperatures up to 1527 degrees Cent. (2780 degrees Fahr.). Extrapolation of Bryant's data over the short interval to 1580 degrees Cent. (2875 degrees Fahr.) yields a value of 3.82 for K_3 , which is in remarkably close agreement with the

value of K_3 calculated above directly from experimental data. However, Bryant has recently recalculated the values for K_3 , using molecular heats calculated from spectroscopic data up to 2000°K. His new value for K_3 at 1580 degrees Cent. (2875 degrees Fahr.) is 4.07, which is entirely within the range of experimental error of this work. The agreement between the reported value for the water gas constant and that obtained from the experimental data of Vacher and of the authors, may be considered substantial evidence of the reliability of both investigations.

SUMMARY AND CONCLUSIONS

An experimental study of equilibrium in the reduction of dissolved ferrous oxide by hydrogen at 1600 degrees Cent. (2910 degrees Fahr.) has led to the following conclusions:

The equilibrium constant is independent of the oxygen concentration, and the activity of ferrous oxide dissolved in liquid iron is, therefore, proportional to its per cent by weight.

An unsuspected source of error in previous work has been discovered and corrected, thereby changing the value of the constant from 4.75 to 3.95.

The free energy of formation of ferrous oxide in a 1 per cent solution in liquid iron has been determined to be -34,740 calories at 1600 degrees Cent. (2910 degrees Fahr.).

The value of the carbon-iron oxide product at equilibrium in liquid iron has been calculated to be 0.006, which is considered a confirmation of the experimental value, 0.010.

The value of the constant of the water gas reaction found by combining the present data with Vacher's work is in agreement with that obtained from other sources.

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